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Technical Report No. 2

Pyrrromethene-BF₂ Complexes as Laser Dyes: 2

by

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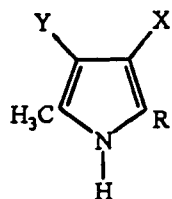
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Pyrromethene-BF₂ Complexes as Laser Dyes: 2

Pyrromethene-BF₂ complexes (P-BF₂) **7** were obtained from α -unsubstituted pyrroles **5** by acylation and condensation to give intermediate pyrromethene hydrohalides **6** followed by treatment with boron trifluoride etherate. Conversion of ethyl α -pyrrolecaboxylates **4** to α -unsubstituted pyrroles **5** was brought about by thermolysis in phosphoric acid at 160 °C, or by saponification followed by decarboxylation in ethanolamine at 180 °C, or as unisolated intermediates in the conversion of esters **4** to pyrromethene hydrobromides **6** by heating in a mixture of formic and hydrobromic acids. Addition of hydrogen cyanide followed by dehydrogenation by treatment with bromine converted 3,5,3',5'-tetramethyl-4,4'-diethylpyrromethene hydrobromide **9** to 3,5,3',5'-tetramethyl-4,4'-diethyl-6-cyanopyrromethene hydrobromide **6bb**, confirmed by the further conversion to 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF₂ complex **7bb** on treatment with boron trifluoride etherate.

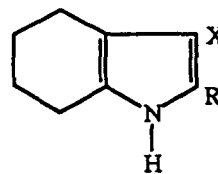
An alternation effect in the relative efficiency (RE) of laser activity in 1,3,5,7,8-pentamethyl-2,6-di-n-alkylpyrromethene-BF₂ dyes depended on the number of methylene units in the n-alkyl substituent, -(CH₂)_nH, to give RE ≥ 100 when $n = 0, 2, 4$ and RE 65, 85 when $n = 1, 3$. (RE 100 arbitrarily assigned to the dye rhodamine-6G). The absence of fluorescence and laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-isopropylpyrromethene-BF₂ complex **7p** and a markedly diminished fluorescence quantum yield (Φ 0.23) and lack of laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-cyclohexylpyrromethene-BF₂ complex **7q** were attributed to molecular nonplanarity brought about by the steric interference between each of the two bulky 8-substituents with the 1,7-dimethyl substituents. An atypically low RE 20 for a peralkylated dye without steric interference was observed for 1,2,6,7-bistrimethylene-3,5,8-trimethylpyrromethene-BF₂ complex **7j**. Comparisons with peralkylated dyes revealed a major reduction in RE for the six dyes **7u-z** lacking substitution at the 8-position.

Low laser activity RE was brought about by functional group (polar) substitution in the 2,6-diphenyl derivative **7l**, RE 20, and the 2,6-diacetamido derivative **7m**, RE 5, of 1,3,5,7,8-pentamethylpyrromethene-BF₂ complex (PMP-BF₂) **7a** and in 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene-BF₂ complex **7n**, RE 30. Diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate-BF₂ complex **7aa**, and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF₂ complex **7bb**, offered examples of P-BF₂ dyes with electron withdrawing substituents at the 8-position. The dye **7aa**, λ_{1as} 617 nm, showed nearly twice the power efficiency that was obtained from rhodamine B, λ_{1as} 611 nm.



4 R = CO₂CH₂CH₃

5 R = H



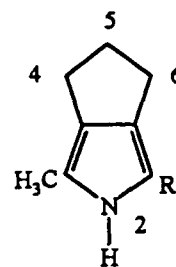
4i X = CH₃, R = CO₂C₂H₅

5h X = R = H

5i X = CH₃, R = H

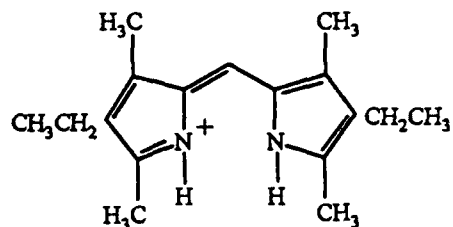
| 4.5 | X | Y |
|-----|---------------------------------|---|
| a | CH ₃ | H |
| b | CH ₃ | CH ₃ |
| c | CH ₃ | CH ₂ CH ₃ |
| d | CH ₃ | (CH ₂) ₂ CH ₃ |
| e | CH ₃ | (CH ₂) ₃ CH ₃ |
| f | CH ₃ | CH(CH ₃) ₂ |
| g | CH ₃ | C(CH ₃) ₃ |
| k | CH ₂ CH ₃ | CH ₂ CH ₃ |
| o | C ₆ H ₅ | CH ₂ CH ₃ |
| p | C ₆ H ₅ | C ₆ H ₅ |
| q | C ₆ H ₅ | COCH ₃ |

| 5 | X | Y |
|---|------------------|-------------------------------|
| l | CH ₃ | C ₆ H ₅ |
| m | CH ₃ | NHCOCH ₃ |
| n | OCH ₃ | CH ₃ |

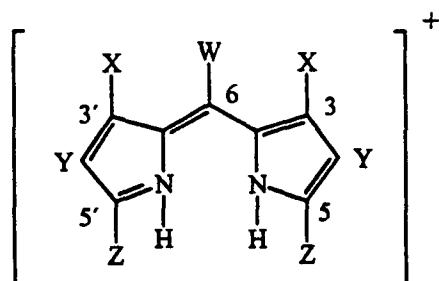


4j R = CO₂C₂H₅

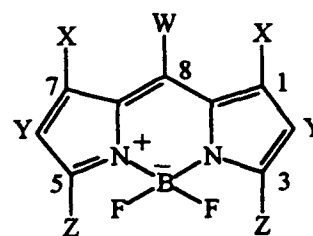
5j R = H



Br⁻



6

 A^- 

7

| 6,7 | W | X | Y | Z | A |
|-----|--|--|---|-----------------|----|
| a | CH ₃ | CH ₃ | H | CH ₃ | Cl |
| b | CH ₃ | CH ₃ | CH ₃ | CH ₃ | Cl |
| c | CH ₃ | CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| d | CH ₃ | CH ₃ | (CH ₂) ₂ CH ₃ | CH ₃ | Cl |
| e | CH ₃ | CH ₃ | (CH ₂) ₃ CH ₃ | CH ₃ | Cl |
| f | CH ₃ | CH ₃ | CH(CH ₃) ₂ | CH ₃ | Cl |
| g | CH ₃ | CH ₃ | C(CH ₃) ₃ | CH ₃ | Cl |
| h | CH ₃ | H | ————(CH ₂) ₄ ———— | | Cl |
| i | CH ₃ | CH ₃ | ————(CH ₂) ₄ ———— | | Cl |
| j | CH ₃ | ————(CH ₂) ₃ ———— | | CH ₃ | Cl |
| k | CH ₃ | CH ₂ CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| l | CH ₃ | CH ₃ | C ₆ H ₅ | CH ₃ | Cl |
| m | CH ₃ | CH ₃ | NHCOCH ₃ | CH ₃ | Cl |
| n | CH ₃ | OCH ₃ | CH ₃ | CH ₃ | Cl |
| o | CH ₂ CH ₃ | CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| p | CH(CH ₃) ₂ | CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| q | <i>c</i> -C ₆ H ₁₁ | CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| r | CH ₂ OCOCH ₃ | CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| s | <i>p</i> -(CH ₃) ₂ NC ₆ H ₅ | CH ₃ | CH ₂ CH ₃ | CH ₃ | Cl |
| t | <i>p</i> -CH ₃ OC ₆ H ₅ | CH ₃ | H | CH ₃ | Cl |
| u | H | C ₆ H ₅ | CH ₂ CH ₃ | CH ₃ | Br |
| v | H | C ₆ H ₅ | C ₆ H ₅ | CH ₃ | Br |
| w | H | C ₆ H ₅ | H | CH ₃ | Br |
| x | H | CH ₃ | C(CH ₃) ₃ | CH ₃ | Br |
| y | H | CH ₂ CH ₃ | CH ₂ CH ₃ | CH ₃ | Br |
| z | H | CH ₃ | CH ₃ | CH ₃ | Br |
| aa | CN | CH ₃ | CO ₂ CH ₂ CH ₃ | CH ₃ | Br |
| bb | CN | CH ₃ | CH ₂ CH ₃ | CH ₃ | Br |